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Thermochemical properties of 1-butyl-3-methylimidazolium nitrate

A.A. Strechan [a], A.G. Kabo [a], Y.U. Paulechka [a], A.V. Blokhin [a], G.J. Kabo [a,*],
A.S. Shaplov [b], E.I. Lozinskaya [b]

[a] Chemistry Faculty, Belarusian State University, Leningradskaya 14, 220030 Minsk, Belarus
[b] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (INEOS RAS),
GSP-1, 28 Vavilov Street, 119991 Moscow, Russia

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ABSTRACT

Heat capacity for 1-butyl-3-methylimidazolium nitrate [C_4mim][NO_3] in the temperature range (5–370) K has been measured by adiabatic calorimetry. Temperatures and enthalpies of its phase transitions have been determined. Thermodynamic functions have been calculated for the crystalline and the liquid states. Phase transition temperatures for set of nitrate salts have been compared. Enthalpy of combustion and enthalpy of formation for crystalline [C_4mim][NO_3] have been determined using a static-bomb isoperibol combustion calorimeter. A correlation scheme for the estimation of C_p of ionic liquids has been developed.

1. Introduction

The room-temperature ionic liquids with organic cations are very useful for the various technical solutions [1–4]. Their thermodynamic properties are necessary for justification of conditions for the synthesis and use.

Earlier, the authors investigated a series of 1-butyl-3-methylimidazolium ([C_4mim]$^+$) ILs ([C_4mim][PF_6] [5,6], [C_4mim][NTf_2] [7,8], [C_4mim][Br] [9], [C_4mim][Tos] [10], [C_4mim][CF_3COO] and [C_4mim][CH_3COO] [11]) by adiabatic calorimetry. It was found that thermal behavior of ILs is strongly dependent on the nature of the anion. Differences in thermal behavior of substances are expressed in polymorphism of crystals and in ability to form glasses.

The data on $\Delta_c H$ and $\Delta_f H$ for ionic liquids are scarce [12]. This is caused, first of all, by some problems preventing experimental determination of these quantities.

This work is a continuation of our studies on physical properties of ionic liquids. The object of investigation, namely 1-butyl-3-methylimidazolium nitrate [C_4mim][NO_3], was selected due to several factors. At first, this ionic liquid is halogen free and thus, more environmentally friendly. Furthermore, nitrate ionic liquids were successfully utilized as interesting medium for dissolution and stabilization of metal salts [13] and enzymes [14]. Finally [C_2mim][NO_3] was applied as electrolyte for electrochemical capacitors [15]. Here we report low-temperature heat capacities and parameters of phase transitions for [C_4mim][NO_3], based on measurements by adiabatic calorimetry in the temperature range of (5–370) K. The results of determination of combustion energy for [C_4mim][NO_3] in a static-bomb isoperibol combustion calorimeter are presented as well.

2. Experimental

2.1. Sample preparation

The sample of [C_4mim][NO_3] was prepared according to the known procedure [16] by means of the reaction between corresponding imidazolium bromide salt and silver nitrate. The resulting product represents slightly yellow liquid at $T = 298$ K and was carefully dried under vacuum $p \sim 1$ Pa at $T = 333$ K temperature with special P_2O_5 containing water catcher. ^{1}H NMR (400 MHz $(CD_3)_2CO$): $\delta = 0.90$ (t, 3H, $CH_2\underline{CH_3}$, $J_{HH} = 9.72$ Hz), 1.32 (m, 2H, $\underline{CH_2}CH_3$, $J_{HH} = 9.76$ Hz), 1.84 (m, 2H, $\underline{CH_2}CH_2CH_3$, $J_{HH} = 10.3$ Hz), 4.02 (s, 3H, $\underline{NCH_3}$), 4.34 (t, 2H, $J_{HH} = 9.72$ Hz), 7.83 (s, 1H, H5 (Im)), 7.90 (s, 1H, H4 (Im)), 9.56 (s, 1H, H2 (Im)); IR (KBr pellet): 3447 (w), 3144 (m), 3088 (m), 2961 (m), 2874 (m), 2400 (w), 1767 (w), 1573 (s), 1466 (s), 1350 (vs, ν_{NO_3}), 1171 (s), 833 (m, ν_{NO_3}), 755 (w), 653 (w), 624 (m) cm^{-1}; Raman, $\Delta\nu$: 3171 (w), 3104 (w), 2971 (s), 2941 (s), 2916 (s), 2878 (m), 1573 (w), 1422 (s), 1389 (w), 1339 (m), 1117 (w), 1063 (vs, ν_{NO_3}), 882 (w), 832 (w), 707 (w), 628 (w), 598 (w),

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* Corresponding author. Tel.: +375 17 2003916; fax: +375 17 2003916.
E-mail address: kabo@bsu.by (G.J. Kabo).

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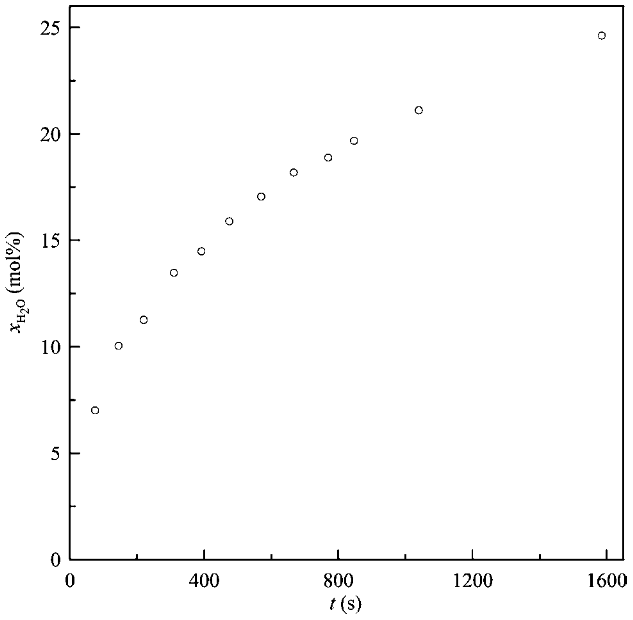

Fig. 1. Kinetics of water absorption from air for [C_4mim][NO_3] at relative humidity of 65% and T = 295 K.

326 (w), 129 (s) cm^{-1}. The initial mass fraction purity of the sample was >99.4 mass%: 47.45% C, 7.20% H, 20.91% N as determined by elemental analysis. Water content was determined by Karl Fischer titration to be 1.6×10^{-2} mass%.

[C_4mim][NO_3] possesses high hygroscopysity. When exposed to air at $T = (295 \pm 1)$ K and relative humidity of 65%, this compound absorbed ≈10 mol% of water during the first 3 min (Fig. 1). The sample was handled in a dry box. In order to remove the residue of water [C_4mim][NO_3] was dried over P_2O_5 during 2 weeks prior to the heat capacity measurements. The mole fraction purity x of [C_4mim][NO_3] was determined by the fractional melting technique to be 0.981. The experimental data (Table 1) were fitted by the following equation (Fig. 2) [17]:

$$\ln\left(\frac{\nu}{f}+1\right) = \frac{\Delta_{\text{fus}}H^\circ}{RT_{\text{fus}}^2} \times \left(1+\left(\frac{1}{T_{\text{fus}}}-\frac{\Delta C_p(T_{\text{fus}})}{2\Delta_{\text{fus}}H^\circ}\right)(T_{\text{fus}}-T)\right)(T_{\text{fus}}-T), \tag{1}$$

where ν is the amount of impurities in a sample, mole per mole of the main substance; f is the equilibrium melt fraction at temperature T; $\Delta_{\text{fus}}H^\circ$ is the enthalpy of fusion for a pure compound at the triple-point temperature T_{fus} and ΔC_p is the heat-capacity change at fusion of a pure compound.

For combustion measurements, the sample was additionally dried over P_2O_5. The absence of systematic drift for Δ_cH in consecutive combustion experiments separated by a period of 48 h was considered to be a criterion of sufficient removal of water.

2.2. Adiabatic calorimetry

Heat capacities (c_s) in the condensed state in a range of temperatures of (5–370) K and phase-transition enthalpies of [C_4mim][NO_3] were measured in a Termis TAU-10 adiabatic calorimeter. The calorimeter and the procedure of measurements were described in [18].

Table 1
Results of fractional melting for [C_4mim][NO_3], crystal I[a]

T (K)	f
Crystal I	
Series 1	
305.565	0.2342
306.307	0.2956
306.838	0.3648
307.225	0.4395
307.511	0.5179
307.730	0.5989
307.918	0.6810
$T_{\text{fus}} = (309.16 \pm 0.03)$ K	
$x = (0.981 \pm 0.001)$	
Series 2	
305.628	0.2439
306.350	0.3057
306.874	0.3752
307.252	0.4507
307.532	0.5291
307.746	0.6099
307.913	0.6924
308.061	0.7756
$T_{\text{fus}} = (309.15 \pm 0.02)$ K	
$x = (0.981 \pm 0.001)$	

[a] T_{fus} is the triple point temperature of the compound and x is the mole fraction purity of the sample.

2.3. Bomb combustion calorimetry

Combustion enthalpy for [C_4mim][NO_3] was measured in a home-made isoperibol calorimeter with air bath. The calorimetric container was equipped with a vacuum shell [19]. The shell was thermostated within ±0.02 K. A Pt500 thermometer was used as a temperature sensor in the shell and the calorimetric container. The bomb volume was 95 cm^3. The energy equivalent of the calorimeter, $\varepsilon(\text{calor}) = (9826.0 \pm 3.2)\,J\,K^{-1}$ (with taking into account the uncertainty of benzoic acid), was obtained in a series of 10 calorimetric experiments with benzoic acid (K-2 grade, mass-fraction purity of 0.99993) having a certified value of the combustion energy

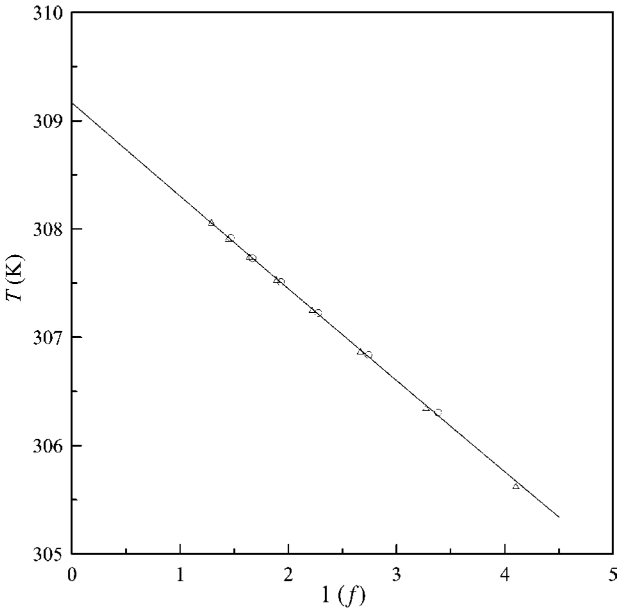

Fig. 2. Results of the fractional-melting experiments for [C_4mim][NO_3]: ○, series 1 and △, series 2.

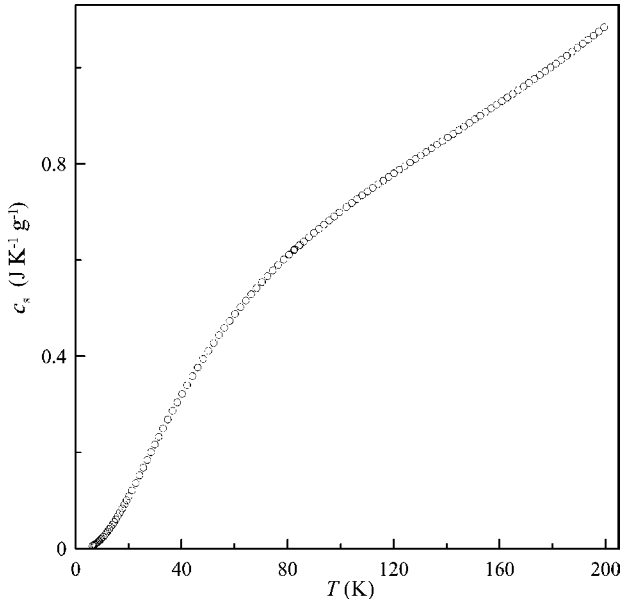

Fig. 3. Experimental heat capacity for $[C_4mim][NO_3]$ in the temperature range of (5–200) K: series 5 from 5 to 80 K; series 2 from 80 to 200 K.

under standard conditions, $\Delta_C u°(\text{cr}, 298.15\,\text{K}) = -(26{,}414 \pm 5)\,\text{J g}^{-1}$, for mass in vacuum. The combustion of the ionic liquid was carried out in polyethylene bags. The combustion energy for polyethylene was determined in an independent series of experiments to be $\Delta_C u°(298.15\,\text{K}) = -46.30 \pm 0.04\,\text{kJ g}^{-1}$, that is in a good agreement with the value presented in [20]. Cotton thread was used for ignition $\Delta_C u°(\text{cot. thread}, 298.15\,\text{K}) = -16.95\,\text{kJ g}^{-1}$ [20].

3. Results and discussion

3.1. Heat capacity of $[C_4mim][NO_3]$

The experimental c_s values for $[C_4mim][NO_3]$ in the temperature range of (5–370) K are presented in Figs. 3 and 4 and Table A.1.

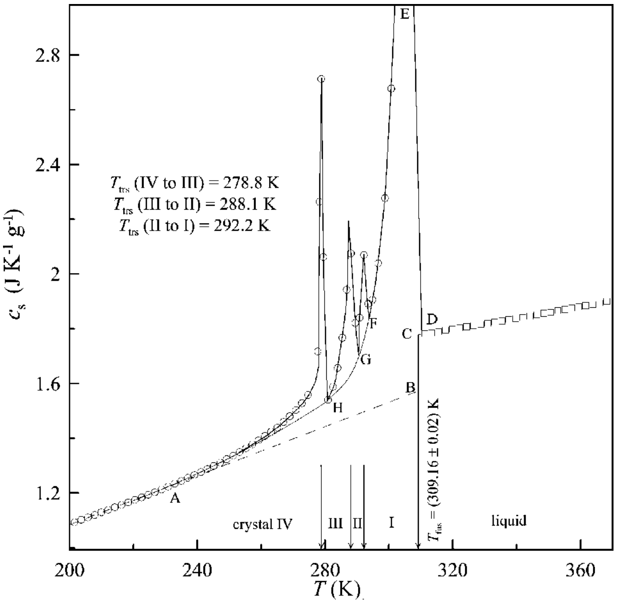

Fig. 4. Solid-phase phase transitions for $[C_4mim][NO_3]$ in the temperature range of (260–310) K.

Table 2
Determination of the molar enthalpy of fusion for crystal of $[C_4mim][NO_3]$

Series number	T_{start} (K)	T_{end} (K)	Q (J mol^{-1})	$\Delta_{fus}H_m°$ (J mol^{-1})	$\Delta_{fus}S_m°$ (J K^{-1} mol^{-1})
1	230.00	311.08	40,892	17,972^a	
2	230.00	311.37	41,051	18,027^a	
3	230.00	312.18	41,288	17,974^b	
Average				(17,991 ± 78)	(58.19 ± 0.25)

[a] From the fractional melting experiments.
[b] From the ordinary heat capacity experiments.

Liquid $[C_4mim][NO_3]$ supercooled on cooling from 370 K. Crystallization of the sample began at 272 K. Heat evolution due to the crystallization ceased at ~290 K and after that the sample was heated to $T = 300$ K. After annealing at the latter temperature for 7 h, the crystal of $[C_4mim][NO_3]$ was formed. Then, the sample was cooled to 77 K, and its heat capacity was measured to 370 K (series 1). In the further series of measurements the crystal of $[C_4mim][NO_3]$ was obtained similarly (series 2–4).

The ability of the sample to supercool allowed us to measure heat capacity of the supercooled liquid from 274 K to T_{fus} (series 5). The heat capacities of the supercooled liquid $[C_4mim][NO_3]$ are presented in Table A.1 and described by Eq. (2) calculated from experimental heat capacities in a range of (274–370) K.

$$C_{p,m}(\text{liquid})\,(\text{J K}^{-1}\,\text{mol}^{-1}) = 284.0 + 8.94 \times 10^{-2}T\,(\text{K}) + 4.816 \times 10^{-4}T^2\,(\text{K}) \qquad (2)$$

3.2. Solid-phase transitions and fusion

Three solid-phase transitions in the heat-capacity curve were found in the temperature range of (250–300) K (Fig. 4). The transition temperature corresponding to the maximum in the ($C_{s,m}$ vs. T) curve are: $T_{trs}(\text{crIV} \rightarrow \text{crIII}) = 278.8$ K; $T_{trs}(\text{crIII} \rightarrow \text{crII}) = 288.1$ K; $T_{trs}(\text{crII} \rightarrow \text{crI}) = 292.2$ K. The enthalpies of transitions were determined by integration of the C_p minus AHGFE curve (Fig. 4) were found to be $\Delta_{trs}H°$ (crIV → crIII) = 2.08 kJ mol^{-1}; $\Delta_{trs}H°$ (crIII → crII) = 0.36 kJ mol^{-1}; $\Delta_{trs}H°$ (crII → crI) = 0.15 kJ mol^{-1}. AHGFE (Fig. 4) is the melting line for crI $[C_4mim][NO_3]$.

The fusion enthalpy for $[C_4mim][NO_3]$ (Table 2) was calculated as the area ABCDEFGH (Fig. 4) using the following equation:

$$\Delta_{fus}H_m^{\circ} = Q - \int_{T_{start}}^{T_{fus}} C_{p,m}(\text{cr})\,dT - \int_{T_{fus}}^{T_{end}} C_{p,m}(\text{liq})\,dT - \sum_i \Delta_{trs}H_{i,m}^{\circ} \qquad (3)$$

where Q is the energy required to heat one mole of substance from T_{start} to T_{end}; $\Delta_{trs}H_{i,m}°$ is the enthalpy of the ith phase transition in a range of (250–300) K.

The initial T_{start} and final T_{end} temperatures lay outside the melting range. Heat capacity of the crystal was described by the following equation:

$$C_{p,m}(\text{crystal})\,(\text{J K}^{-1}\,\text{mol}^{-1}) = 38.05 + 0.9007T\,(\text{K}) \qquad (4)$$

obtained from the experimental heat capacities in the temperature range of (200–232) K for crystal.

The fusion enthalpy is $\Delta_{fus}H_m° = (17.99 \pm 0.08)\,\text{kJ mol}^{-1}$. The fusion temperature is $T_{fus} = (309.16 \pm 0.02)$ K.

Similar solid-phase transitions were observed earlier for ammonium [21–24], rubidium [25–27], thallium [28–30] and silver [31–33] nitrates (Table 3). Lucas and Shamsuzzoha [27] demonstrated that in rubidium nitrate transitions (IV–III–II) deal with a

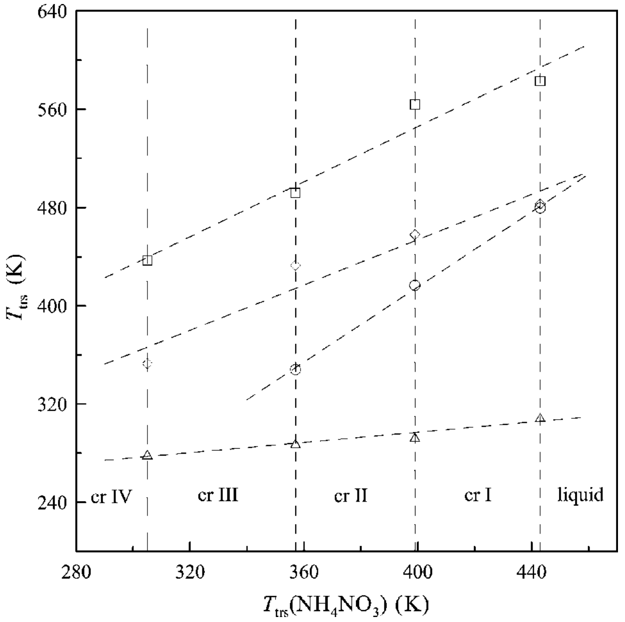

Fig. 5. Correlation between solid-phase transition temperatures in a series of nitrate salts: △, $[C_4mim][NO_3]$; □, $RbNO_3$; ○, $TlNO_3$; ◇, $AgNO_3$.

minor alteration in the sublattice of rubidium atoms at transition from pseudo-cubic into cubic lattice, and nitrate anions change from being orientationally ordered to disordered in the given structures. Transition III to II is probably due to re-orientation of nitrate anions, rather than changes in the Rb atoms sublattice [27].

Similar anomalies in thermal behavior have not been observed for earlier investigated 1-butyl-3-methylimidazolium ionic liquids [6,8–11]. Therefore, appearance of the solid-phase transitions in $[C_4mim][NO_3]$ is related to evolution of spatial orientations of the nitrate ion.

We analyzed the phase transition temperatures for set of nitrates having three solid-phase transitions. The correlation between T_{trs} and T_{fus} in the series of salts with nitrate anion was found. As shown in Fig. 5, the dependence of $T_{trs\cdot i}$ vs. ($T_{trs\cdot i}$ in a reference substance NH_4NO_3) is linear.

A similar trend for entropies of phase transitions for the substances presented in Table 3 was found.

3.3. Thermodynamic properties

The smoothed values of thermodynamics functions for $[C_4mim][NO_3]$ in the crystalline and liquid states are presented in Table 4 ($M = 201.223\ \mathrm{g\ mol^{-1}}$ using atomic masses from [34]). The standard thermodynamic functions of $[C_4mim][NO_3]$ at $T = 298.15$ K are equal to:

$$C_{p,\mathrm{m}} = (305.8 \pm 1.2)\ \mathrm{J\ K^{-1}\ mol^{-1}}, \quad \Delta_0^T S_\mathrm{m}^\circ = (365.8 \pm 1.5)\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$\frac{\Delta_0^T H_\mathrm{m}^\circ}{T} = (180.3 \pm 0.7)\ \mathrm{J\ K^{-1}\ mol^{-1}}, \quad \Phi_\mathrm{m}^\circ = (185.5 \pm 1.7)\ \mathrm{J\ K^{-1}\ mol^{-1}}.$$

3.4. Enthalpy of formation

The results of determination of the combustion energy for $[C_4mim][NO_3]$ are listed in Table 5. The average molar energy of combustion at 298.15 K is

$$\Delta_c U_\mathrm{m}^\circ(\mathrm{cr}) = -(5011.4 \pm 2.9)\ \mathrm{kJ\ mol^{-1}}.$$

for the combustion reaction of $[C_4mim][NO_3]$ is

$$C_8H_{15}N_3O_3(\mathrm{cr}) + \tfrac{41}{4}O_2(\mathrm{g}) = 8CO_2(\mathrm{g}) + \tfrac{15}{2}H_2O(\mathrm{liq}) + \tfrac{3}{2}N_2(\mathrm{g}) \qquad (5)$$

Taking into account the stoichiometric coefficients of Eq. (5), the combustion enthalpy is equal to:

$$\Delta_c H_\mathrm{m}^\circ(\mathrm{cr}) = -(5013.2 \pm 2.9)\ \mathrm{kJ\ mol^{-1}}.$$

The formation enthalpy of the compound:

$$\Delta_f H_\mathrm{m}^\circ(\mathrm{cr}, 298.15) = -(278.6 \pm 2.5)\ \mathrm{kJ\ mol^{-1}}$$

was calculated from Eq. (5) based on the formation enthalpies: $\Delta_f H^\circ(CO_2;\ \mathrm{g}) = -(393.51 \pm 0.13)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_f H^\circ(H_2O;\ \mathrm{liq}) = -(285.80 \pm 0.04)\ \mathrm{kJ\ mol^{-1}}$ [35].

Table 3
The parameters of solid-to-solid transitions for a set of compounds

Compound	Transition	T (K)	$\Delta_{trs}H_m^\circ$ (kJ mol^{-1})	$\Delta_{trs}S_m^\circ$ (J K^{-1} mol^{-1})	$\sum_i \Delta_{trs}H_{m,i}^\circ$ (kJ mol^{-1})	$\sum_i \Delta_{trs}S_{m,i}^\circ$ (J K^{-1} mol^{-1})
$[C_4mim][NO_3]$[a]	crIV to crIII	279	2.08	7.5	2.59	9.2
	crIII to crII	288	0.36	1.2		
	crII to crI	292	0.15	0.5		
	crI to liquid	309	17.99	58.2		
$RbNO_3$ [25–27]	crIV to crIII	437	3.89	8.9	8.07	17.1
	crIII to crII	492	3.22	6.5		
	crII to crI	564	0.96	1.7		
	crI to liquid	583	4.6	7.9		
NH_4NO_3 [21–24]	crIV to crIII	305	1.70	5.6	7.49	20.5
	crIII to crII	357	1.35	3.8		
	crII to crI	399	4.44	11.1		
	crI to liquid	443	6.40	14.4		
$TlNO_3$ [28–30]	crIV to crIII	–	–	–	4.35	10.9
	crIII to crII	348	1.00	2.9		
	crII to crI	417	3.35	8.0		
	crI to liquid	480	9.46	19.7		
$AgNO_3$ [21–33]	crIV to crIII	353	n/a[b]	n/a	n/a	n/a
	crIII to crII	433	2.47	5.7		
	crII to crI	458	n/a	n/a		
	crI to liquid	483	12.13	25.1		

[a] This work.

[b] Not available data.

Table 4

Thermodynamic properties for $[C_4mim][NO_3]$ ($R = 8.31447\ \mathrm{J\,K^{-1}\,mol^{-1}}$)

T (K)	$C_{p,\mathrm{m}}/R$	$\Delta_0^T H_\mathrm{m}^\circ/RT$	$\Delta_0^T S_\mathrm{m}^\circ/R$	Φ_m°/R
Crystal IV				
5	0.0645	0.0162	0.0216	0.0054
10	0.536	0.138	0.183	0.045
15	1.435	0.410	0.558	0.148
20	2.615	0.810	1.128	0.318
25	3.933	1.301	1.851	0.550
30	5.268	1.851	2.687	0.835
35	6.548	2.432	3.596	1.164
40	7.757	3.023	4.550	1.527
45	8.886	3.612	5.530	1.917
50	9.933	4.193	6.521	2.328
55	10.90	4.759	7.513	2.754
60	11.78	5.308	8.500	3.192
70	13.36	6.348	10.44	4.089
80	14.72	7.311	12.31	5.001
90	15.90	8.201	14.12	5.914
100	16.96	9.025	15.85	6.821
110	17.94	9.792	17.51	7.718
120	18.87	10.51	19.11	8.601
130	19.77	11.19	20.66	9.469
140	20.66	11.83	22.16	10.32
150	21.54	12.45	23.61	11.16
160	22.43	13.05	25.03	11.98
170	23.34	13.63	26.42	12.79
180	24.29	14.19	27.78	13.59
190	25.27	14.75	29.12	14.37
200	26.29	15.30	30.44	15.14
210	27.34	15.85	31.75	15.90
220	28.41	16.39	33.04	16.65
230	29.48	16.94	34.33	17.39
240	30.55	17.49	35.61	18.12
250	31.62	18.03	36.88	18.85
260	32.69	18.57	38.14	19.56
270	33.76	19.12	39.39	20.27
278.2	34.64	19.56	40.41	20.85
Crystal III				
278.2	34.64	20.46	41.31	20.85
280	34.83	20.55	41.53	20.99
285	35.37	20.80	42.16	21.35
288.1	35.70	20.96	42.54	21.58
Crystal II				
288.1	35.70	21.11	42.69	21.58
290	35.91	21.21	42.93	21.72
292.2	36.14	21.32	43.20	21.88
Crystal I				
292.2	36.14	21.38	43.26	21.88
295	36.44	21.53	43.61	22.08
298.15	36.78	21.68	44.00	22.31
300	36.98	21.78	44.22	22.45
309.16	37.96	22.24	45.35	23.11
Liquid				
309.16	43.02	29.24	52.35	23.11
310	43.06	29.28	52.47	23.19
320	43.52	29.72	53.84	24.12
330	43.99	30.14	55.19	25.04
340	44.48	30.56	56.51	25.95
350	44.99	30.96	57.81	26.84
360	45.52	31.36	59.08	27.72
370	46.06	31.75	60.33	28.58

Table 5

Determination of the standard molar combustion energy for $[C_4mim][NO_3]$ at 298.15 K[a]

	Number			
	1	2	3	4
m (g)	0.28559	0.33631	0.28035	0.16922
m'(aux) (g)	0.04446	0.05266	0.04804	0.05720
m''(aux) (g)	0.00165	0.00162	0.00166	0.00210
$p(O_2)$ (MPa)	3.04	3.04	3.04	3.04
t_i (°C)	25.04021	25.03837	25.02342	25.02231
t_f (°C)	26.06279	26.22699	26.05138	25.80904
ΔT_corr (K)	0.93846	1.10517	0.94148	0.70369
K ($\times 10^5\,\mathrm{s^{-1}}$)	2.11	2.03	2.07	2.07
ε^i ($\mathrm{J\,K^{-1}}$)	7.49	7.58	7.49	7.34
ε^f ($\mathrm{J\,K^{-1}}$)	8.06	8.26	8.07	7.77
$-m'\Delta_\mathrm{c}u'$ (J)	2058.5	2438.16	2224.25	2648.36
$-m''\,\Delta_\mathrm{c}u''$ (J)	27.96	27.45	28.13	35.58
$\Delta_\mathrm{ing}U$ (J)	0.20	0.35	0.38	0.35
$\varepsilon_\mathrm{calor}(-\Delta T_\mathrm{corr})$ (J)	−9221.27	−10859.4	−9250.97	−6914.45
$\varepsilon_\mathrm{cont}(-\Delta T_\mathrm{corr})$ (J)	−7.58	−9.15	−7.61	−5.48
$\Delta_\mathrm{IBP}U$ (J)	−9228.66	−10868.2	−9258.2	−6919.58
$\Delta U(HNO_3)$ (J)	21.20	22.52	18.57	17.74
$\Delta_\mathrm{st.state}U$ (J)	5.81	7.02	5.81	3.88
$\Delta_\mathrm{c}u^\circ$ ($\mathrm{J\,g^{-1}}$)	−24,914	−24,897	−24,903	−24,903
$\Delta_\mathrm{c}U_\mathrm{m}^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	−5013.36	−5009.91	−5011.05	−5011.06
$\left\langle \Delta_\mathrm{c}U_\mathrm{m}^\circ(298.15\,\mathrm{K})\right\rangle = (-5011.4 \pm 2.9)\,\mathrm{kJ\,mol^{-1}}$				

[a] m is the mass of the sample of the investigated compound adjusted to vacuum conditions; m' is the mass of the auxiliary substance (polyethylene film) adjusted to vacuum conditions; m'' is the mass of the auxiliary substance used for igniting the sample (cotton thread); $p(O_2)$ is the pressure of oxygen in the bomb; t_i and t_f are the initial and final temperature in the reaction period; ΔT_corr is the corrected temperature rise; K is the cooling constant of the calorimeter; ε^i and ε^f are the energy equivalent of the contents of the bomb in the initial and final states, respectively; $\Delta_\mathrm{c}u'$ is the specific combustion energy of the auxiliary compound; $\Delta_\mathrm{ign}U$ is the electrical energy for igniting the sample; $\varepsilon_\mathrm{calor}$ is the energy equivalent of the calorimeter; $\varepsilon_\mathrm{cont}(-\Delta T_\mathrm{corr}) = \varepsilon^\mathrm{i}(T_i - 298.15) + \varepsilon^\mathrm{f}(298.15 - T_i - \Delta T_\mathrm{corr})$; $\Delta_\mathrm{IBP}U$ is the change of internal energy for the isothermal bomb process; $\Delta U(HNO_3)$ is the energy required for decomposition of the HNO_3 solution formed; $\Delta_\mathrm{st.state}U$ is the energy correction to the standard state (the sum of Washburn's corrections).

3.5. *Comparison of physicochemical properties of $[C_4mim]^+$ ionic liquids*

Physicochemical properties for set of ionic liquids are presented in Table 6. The analysis of these data revealed some empirical trends:

1. Density of a $[C_4mim]^+$ ionic liquid increases with the increase in molar mass of its.
2. The highest specific enthalpy and entropy of fusion and fusion temperature is observed for $[C_4mim][Br]$ while $[C_4mim][NTf_2]$ possesses the lowest $\Delta_\mathrm{fus}H^\circ$, $\Delta_\mathrm{fus}S^\circ$ and T_fus.
3. For hydrophilic liquids ($[C_4mim][CF_3COO]$ and $[C_4mim][Br]$) the ratio of glass transition and fusion temperatures is $T_g/T_\mathrm{fus} \sim 0.62$, that is markedly less than the empirical ratio $T_g/T_\mathrm{fus} = 0.67$ [36].

3.6. *Heat capacity of ionic liquids as a function of molar volume $C_p = f(V_m)$*

The variety of ionic liquids and difficulties in experimental determination of their physicochemical properties makes the search of simple correlation schemes for prediction of their properties especially actual. Earlier [7], the correlation of vaporization enthalpy with surface tension and density was proposed for ionic liquids. We have offered a way of calculation of total heat capacity for ionic liquids from their molar masses and frequencies of normal vibrations for corresponding cations and anions [11].

In the present work we correlated heat capacity C_p of methylimidazolium ionic liquids and their molar volume at $T = 298.15$ K:

$$C_{p,\mathrm{m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = A\left[V_\mathrm{m}\,(\mathrm{m^3\,mol^{-1}}) - 2.56 \times 10^{-4}\right] + B \qquad (6)$$

where $A = (1.75 \pm 0.05) \times 10^6$ and $B = (4.85 \pm 0.04) \times 10^2$ are the coefficients that were found by a least-square method using the dataset for 15 ionic liquids (Fig. 6, Table 7). The correlation coefficient of Eq. (6) is 0.989. The average relative deviation of calculated value from experimental one does not exceed 3%. The standard error of a prediction is $\pm 16\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

Table 6
Physicochemical properties of $[C_4mim]^+$ ionic liquids

Property	Anion						
	$[CF_3COO]^-$ [11,37,38]	$[CH_3COO]^-$ [11,37]	$[NO_3]^-$ (this work [39])	$[Br]^-$ [9,40]	$[PF_6]^-$ [6,38,41]	$[Tos]^-$ [10]	$[NTf_2]^-$ [8,18,38,42]
T_{fus} (K)	296.42	(305)[a]	309.16	351.35	283.51	343.89	270.22
T_g (K)	187.1	203.6	–	218.9	190.6	–	181.5
T_d (K)	415–449	~446	n/a	~546	~700	Above 470	696–712
$\frac{T_g}{T_{fus}}$	0.63	–	–	0.62	0.67	–	0.67
$\Delta_g^l C_{s,m}(T_g)$ ($J\,K^{-1}\,mol^{-1}$)	106.9	112.5	–	84.2	81.6	–	155.4
$\Delta_g^l c_{s,m}(T_g)$ ($J\,K^{-1}\,g^{-1}$)	0.42	0.57	–	0.38	0.29	–	0.37
$\Delta_{fus}H_m$ ($kJ\,mol^{-1}$)	19.34	–	17.99	22.88	19.59	21.57	23.8
$\Delta_{fus}S_m$ ($J\,K^{-1}\,mol^{-1}$)	65.25	–	58.19	65.12	69.10	62.72	88.08
$\Delta_{fus}h$ ($J\,g^{-1}$)	76.69	–	89.40	104.43	68.93	69.49	56.75
$\Delta_{fus}s$ ($J\,K^{-1}\,g^{-1}$)	0.259	–	0.289	0.297	0.243	0.202	0.21
$C_{s,m}$(298.15 K) ($J\,K^{-1}\,mol^{-1}$)	408.8	383.2	305.8[b]	241.6[b]	408.7	411.8[b]	565.1
c_s(298.15 K) ($J\,K^{-1}\,g^{-1}$)	1.621	1.933	1.520	1.103	1.438	1.327	1.347
C_s(360 K) ($J\,K^{-1}\,mol^{-1}$) (liquid)	438.8	420.2	378.5	336.3	446.3	556.0	600.1
c_s(360 K) ($J\,K^{-1}\,g^{-1}$) (liquid)	1.740	2.120	1.881	1.535	1.570	1.791	1.431
ρ ($g\,cm^{-3}$)	1.215	n/a	1.159	n/a	1.366	n/a	1.438
M ($g\,mol^{-1}$)	252.2	198.2	201.2	219.1	284.2	310.4	419.4

[a] Estimated using an empirical rule [36].
[b] Crystal.

Table 7
Training set of ILs used for calculating the coefficients of the correlation equation (6)

Compound	M ($g\,mol^{-1}$)	C_p(298 K) ($J\,K^{-1}\,mol^{-1}$)	ρ(298 K) ($kg\,m^{-3}$) [40,41,44]	$V_m \times 10^3$(298 K) ($m^3\,mol^{-1}$)	C_s(298 K) ($J\,K^{-1}\,mol^{-1}$) (calc.)	ε (%)
$[C_4mim][CF_3COO]$	252.2	407.9 [11]	1215	0.2075	404.6	−0.8
$[C_4mim][NO_3]$	201.2	353.5	1159	0.1736	345.2	−2.3
$[C_4mim][PF_6]$	284.2	407.6 [6]	1366	0.2080	405.4	−0.5
$[C_4mim][NTf_2]$	419.4	565.1 [8,18]	1438	0.2917	551.8	−2.4
$[C_4mim][CF_3SO_3]$	288.2	435.2 [40]	1300	0.2217	429.4	−1.3
$[C_4mim][N(CN)_2]$	205.3	364.5 [40]	1058	0.1940	381.0	4.5
$[C_6mim][BF_4]$ [43]	254.1	417.8 [43]	1101[a]	0.2308	445.3	6.6
$[C_8mim][BF_4]$ [43,44]	282.1	509.1 [43]	1092	0.2583	493.4	−3.1
$[C_8mim][NTf_2]$	475.5	692.7 [45,46]	1321	0.3599	671.2	−3.1
$[C_6mim][NTf_2]$	447.4	629.6 [45,47]	1364	0.3280	615.3	−2.3
$[C_4mim][BF_4]$	226.0	365.1 [40,48]	1204	0.1877	369.9	1.3
$[C_{14}mim][NTf_2]$	559.6	885.9[b] [47]	1131	0.4948	907.2	2.4
$[C_2mim][NTf_2]$	391.3	505.7 [40,45]	1520	0.2575	491.9	−2.7
$[C_2mim][BF_4]$	198.0	308.1 [45,48]	1300[b]	0.1523	307.9	−0.1
$[C_4mmim][PF_6]$	298.2	434.3 [40]	1238	0.2408	462.8	6.6

[a] Interpolated from homologue series.
[b] Extrapolated to 298 K from high-temperature data.

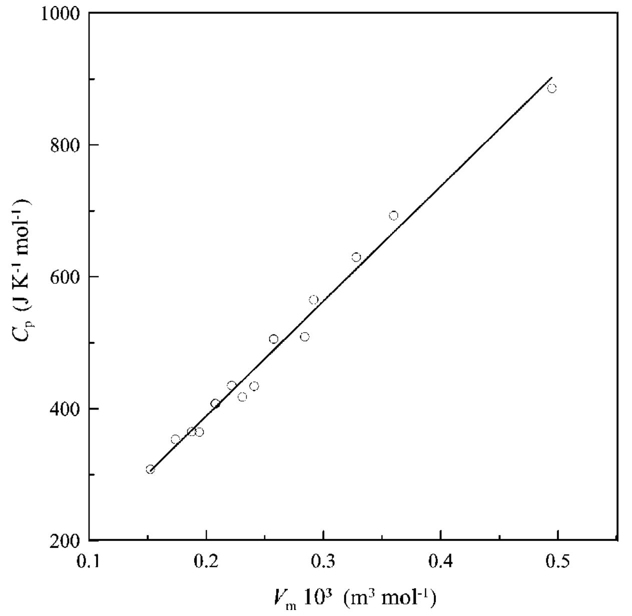

Fig. 6. Ionic liquid heat capacity as a function of the molar volume (T = 298.15 K).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.05.002.

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